Assessing measurement uncertainty on trihalomethanes prediction through kinetic models in water supply systems

Cristiana Di Cristo, Angelo Leopardi and Giovanni de Marinis

ABSTRACT

Disinfection of drinking water through chlorine is commonly used in many countries for reducing pathogenic infection problems, but it may pose a risk to human health due to the formation of some by-products, such as trihalomethanes (THMs). For an adequate management of the disinfection process, it is useful to have models capable of simulating THMs concentrations in water supply systems. However, a crucial aspect is the reliability of their performances when used on real systems and the knowledge of the uncertainty of their predictions. The objective of the present paper is to investigate the simulation of THMs formation through calibrated kinetic models, along with the assessment of the measurement uncertainty on the parameters' estimate and on the model predictions. In particular, a first-order, a second-order and a two-phase kinetic model are considered, while the effect of measurement uncertainty is mainly investigated through the first-order second moment (FOSM) method. The analysis performed on a real case study shows that the three considered models have similar performances in terms of predicted concentrations, which suggests using the simplest first-order one. Moreover, the FOSM results reveal that the first-order model is less affected by measurement uncertainty.

Key words | calibration, chlorine, trihalomethanes, uncertainty, water quality, water supply systems

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INTRODUCTION

Safe drinking water is a high priority, and water supply systems have to provide water without health risks and with prefixed quality requirements. Moreover, consumers' concerns and complaints about the quality of tap water are becoming highly important for water companies and they should always be addressed, when possible. For these reasons it is crucial to develop strategies and methodologies for improving drinking water security by deliberate (Di Cristo *et al.* 2011) or accidental (Di Cristo & Leopardi 2008) contaminations and by phenomena which can determinate quality deterioration through the distribution systems.

In this framework, to make drinking water safe from pathogenic microorganisms, chlorine is commonly used as a disinfectant in water supply systems (WSS) due to its excellent performance and low cost. Chlorine, typically applied as a solution of either sodium or calcium hypochlorite, is a strong oxidizing agent and it reacts with the natural organic matter (NOM) in water, decaying and forming disinfection by-products (DBPs). More than 600 DBPs have been identified and classified (Richardson *et al.* 2002; Shanks *et al.* 2013) and their occurrence in kind and quantity depend on many factors which influence the reaction (e.g., Liang & Singer 2003; Sohn *et al.* 2006).

In this paper the attention is focused on trihalomethanes (THMs), because epidemiological and toxicological studies have suggested that they are human carcinogens and have chronic and subchronic effects upon human health

(Weinberg *et al.* 2002; Nieuwenhuijsen *et al.* 2009). As THMs are volatile, individuals are also exposed to them through inhalation and dermal absorption, during activities such as showering or bathing (Semerarijan & Dennis 2007; Chowdhury *et al.* 2009).

For these reasons, there are regulatory limits on total THMs concentration in tap water, which have to be met at remote distribution system locations where the water residence time and then the THMs concentrations are higher. In summary, while a minimum level of chlorine residual must be maintained in the distribution system to preserve the quality of treated water with respect to microbial regrowth, the total THMs concentration has to be maintained within regulation limits. To comply with these quality standards, it is essential to have models able to reproduce THMs formation in water supply systems, in order to identify management strategies (Cozzolino *et al.* 2005; Radhakrishnan *et al.* 2012).

Numerous studies have been performed for proposing THMs predictive models, usually classified in empirical and kinetic models (Chowdhury & Champagne 2009). The former are based on empirical relationships among the total THMs concentration and certain parameters, which influence their formation, developed using laboratory or field data (e.g., Amy *et al.* 1998; Sohn *et al.* 2004). Di Cristo *et al.* (2013) compared different empirical models in order to investigate their applicability to a water supply system. In particular, the authors individuated the more suitable empirical models, analyzing their ability in reproducing THMs concentrations in real situations, different from those considered for their elaboration. The alternative is to use models based on kinetics involved during chlorine reactions (Adin *et al.* 1991; Clark 1998; Gang *et al.* 2002; Sohn *et al.* 2004), but in this case the kinetic parameters have to be quantified. For many models (Adin *et al.* 1991; Clark & Sivaganesan 1998, 2001; Sohn *et al.* 2004) there are empirical relationships for estimating the THMs formation kinetic coefficient, relating their values with parameters influencing the transformation. However, their applicability to a real case study requires a previous verification that the results represent correctly the system under investigation. Another possibility is to estimate the kinetic parameters using an automated calibration procedure, relating computed and measured chlorine and/or THMs concentration values (Lin & Yeh 2005; Shang & Uber 2007).

While the calibration of chlorine decay parameters has been widely investigated (Powell *et al.* 2000; Al-Omari & Chaudhry 2001), little research has been done for the THMs production rate (Courtis *et al.* 2009). In particular, errors in measuring concentrations result in uncertainty in the estimate of the calibrated parameters and then in the model predictions, which has to be quantified for a reliable use of the water quality simulation. While the uncertainty effect has been previously considered in hydraulic calibrations (Revelli & Ridolfi 2002; Kapelan *et al.* 2005; Alvisi & Franchini 2010), in network design (Bhave & Gupta 2004; Giustolisi *et al.* 2009; Fu & Kapelan 2011), and pollution source identification (Di Cristo & Leopardi 2007; Preis & Ostfeld 2011) problems, little work has been done on water quality.

For example, considering chlorine decay simulation, Pasha & Lansey (2010) examined the effect of hydraulic and quality parameters uncertainty on the model predictions using the Monte Carlo (MC) method, noting a strong influence of the wall reaction coefficient. Then, the same authors (Pasha & Lansey 2012) investigated the effect of data uncertainty on both the wall reaction coefficient estimate and the quality of the chlorine concentration predictions. Finally, Idornigie *et al.* (2010) evaluated the effect of variable hydraulic conditions on the DBPs concentration predictions, but no parameter uncertainty was assessed.

The objective of the present paper, which is an extension of the work presented by the authors at the CCWI2013 International Conference (Di Cristo *et al.* 2014), is to investigate the simulation of THMs formation through calibrated kinetic models, along with the assessment of measurement uncertainty on the parameters' estimate and on the model predictions. In the presented analysis, different calibrated kinetic models are considered and the effect of measurement uncertainty is mainly investigated through the first-order second moment (FOSM) method. The analysis is performed on a real-test case, represented by the main trunk of the Aurunci-Valcanneto Water Supply System (AVWSS). Moreover, for verifying the applicability of the FOSM method, a preliminary analysis is performed through the MC method on a literature network with synthetic data.

THM PREDICTION AND PARAMETER ESTIMATION

In the presented study, the performances in predicting THMs formation in a water supply system of different kinetic models are investigated. In particular, a first-order, a second-order, and a two-phase model, described in the next section, are considered. The analysis is performed on the real-test case of the main trunk of the AVWSS, with the disinfection performed using sodium hypochlorite and field measurements realized in an ad hoc campaign. The kinetic parameters are calibrated through an automatic calibration procedure, with a least-squared objective function relating measured and computed residual chlorine and THMs concentrations.

The performed quality simulation considers as reactive constituents chlorine, which decays, and total THMs, which grow in time. The EPANET-MSX software (Shang *et al.* 2008) is adopted for the multi-species quality simulation, in which the kinetic models presented in the next section are implemented. Moreover, advection is assumed to be the only transport mechanism in pipes, while diffusion and dispersion are neglected, as usual in water supply systems. At junction nodes and storage tanks, complete and instantaneous mixing is assumed to occur.

The considered THM kinetic models

Previous studies have shown that THMs formation is strictly related to chlorine reduction (Kavanaugh *et al.* 1980). Therefore, in the framework of the kinetic models, it may be modeled as a function of chlorine consumption (Clark 1998; Boccelli *et al.* 2003; Brown *et al.* 2011), through the following linear relationship:

$$[THM] = [THM]_0 + D([Cl]_0 - [Cl]) \tag{1}$$

where [Cl] and [THM] are the chlorine and THMs concentrations at time t, measured in (mg/l) and (μg/l), respectively; $[Cl]_0$ and $[THM]_0$ are the initial chlorine and THMs concentrations, respectively. D is the THMs formation kinetic parameter (μg/mg), which indicates the THMs productivity in water. In order to predict the THMs concentrations through Equation (1), the actual concentration [Cl] has to be estimated though a chlorine decay model. The simplest is the first-order model as follows:

$$[Cl] = [Cl]_0 e^{-K_1 t} \tag{2}$$

where t is the time (h); K_1 (1/h) is the first-order chlorine decay kinetic parameter, that has to be properly assigned or calibrated, which is the option adopted in the presented application. Alternatively, in combination with Equation (1), Clark (1998) proposed the following second-order model for THMs prediction:

$$[Cl] = [Cl]_0 \left(\frac{1 - K_c}{1 - K_c e^{-ut}} \right) \tag{3}$$

where K_c (dimensionless) and u (1/h) are kinetic parameters, which have to be estimated.

As an alternative, Sohn *et al.* (2004) proposed a two-phase formulation for predicting chlorine decay and THMs formation, which combines two parallel first-order models, representing fast and slow reactions. In particular, chlorine decay is described by the following relationship:

$$[Cl] = [Cl]_0 [A e^{-K_f t} + (1 - A) e^{-K_s t}] \tag{4}$$

where $0 \leq A \leq 1$ (dimensionless) is a weight parameter, K_f (1/h) and K_s (1/h) are the kinetic parameters of the fast and slow chlorine decay reactions, respectively. THMs formation is represented as follows:

$$[THM] = [Cl]_0 \left[A_T (1 - e^{-K_f t}) + B_T (1 - e^{-K_s t}) \right]. \tag{5}$$

The parameters A_T and B_T are related to the kinetic rates of the chlorine decay through the relations $A_T = K_a A / K_f$ and $B_T = K_b A / K_s$, being K_a (μg/(mg h)) and K_b (μg/(mg h)) the THMs formation kinetic parameters. Note that Equation (5) furnishes the quantity of THMs formatted during the time t, which have to be added to the initial THMs concentration, if different from zero. Sohn *et al.* (2004) derived predictive relationships for the estimate of the kinetic parameters, but their applicability range does not cover the conditions of the test case under investigation in this work. For this reason, in the presented analysis they are calibrated. Similarly, regarding the second-order model, even if predictive relationships are available in the literature for K_C,

u, and D (Clark & Sivaganesan 1998), they are calibrated, as done for the other models.

In summary, the formulations investigated in the following are the first- and the second-order models, represented by Equations (2) and (3) considered alternatively in combination with Equation (1), along with the two-phase model, represented by Equations (4) and (5). Their performances in predicting THMs formation and their response with respect to uncertainty are studied. The kinetic parameters of the considered models, listed in Table 1, are estimated through the calibration procedure described in the next section. It is worth noting that for the first-order model the number of the parameters, NP, which have to be calibrated, is two, one for chlorine decay and one for THMs formation. Three parameters have to be evaluated for the second-order model (NP = 3), while the two-phase model requires the estimation of five parameters (NP = 5).

Parameter estimation

The values of the kinetic parameters are obtained by minimizing the following objective function:

$$f = f_{CL} + f_{THM} \quad \text{with} \quad f_{CL} = \sum_{i=1}^{NC} \left(\frac{[Cl]_i^c - [Cl]_i^m}{[Cl]_i^m} \right)^2 \quad \text{and}$$
$$f_{THM} = \sum_{i=1}^{NT} \left(\frac{[THM]_i^c - [THM]_i^m}{[THM]_i^m} \right)^2 \tag{6}$$

where NC and NT are the numbers of the measurements of [Cl] and [THM], respectively; the apexes c and m indicate the calculated and measured concentrations in the measurement point i, respectively. Equation (6) is also subject to the hydraulics equations, which describes the flow in the network, and to the considered water quality model. For solving the presented optimization problem, the EPANET-MSX software is coupled with a gradient-based optimization algorithm. The use of a gradient-based optimization method is well suited for the first-order and the two-phase models, since the objective function has a quadratic form. For the second-order model the objective function is more complex, but it has been tested that the gradient method is rapidly converging to the optimal solution.

The optimization problem expressed by Equation (6) may be solved using a joint or two-steps approach. In the joint calibration, all kinetic parameters are simultaneously estimated considering both chlorine and THMs measurements. In the two-step approach, first the chlorine decay parameters, P_C (Table 1), are calibrated using the residual chlorine measurements and minimizing only the f_{CL} term of Equation (6). Then, fixing them, the THMs formation parameters, P_T (Table 1), are estimated through a second calibration, performed using only the THMs measurements and minimizing f_{THM}. In a previous analysis, Di Cristo *et al.* (2014) have shown that the joint approach does not represent a good option for the second-order model, because it is only sensitive to the chlorine decay parameters K_C and u, and then the simultaneous calibration is not capable of modifying the initial D value. For this reason, the two-step approach is adopted here for all models.

It is worth noting that in applying a THMs formation model to a water system, the kinetic parameters, depending on water quality, operational, and environmental conditions, should theoretically be considered different in different locations. However, unique global values are assumed for the whole system, when the conditions are not very variable, which is the option adopted in the applications presented herein.

UNCERTAINTY ANALYSIS

Among the different methods available for uncertainty analysis, the MC method is widely used. It is a random enumeration technique that generates and evaluates a large number of parameter sets, assuming a distribution of the input parameters (e.g., Rubinstein & Kroese 2008). MC results can be considered correct if a sufficiently large sample size is adopted. Alternative techniques, which require fewer realizations, are based on first-order

Table 1 | Chlorine decay and THMs formation parameters of the considered models

Model	Chlorine decay parameters (P_C)	THMs formation parameters (P_T)
First-order	K_1	D
Second-order	K_c, u	D
Two-phase	A, K_f, K_s	K_a, K_b

approximation, like the FOSM approach. In the present study, the first-order analysis is mainly used for estimating the uncertainty of both the model parameters and predictions, as already presented in the literature for the hydraulic calibration process (Bush & Uber 1998; Lansey *et al.* 2001; Kang & Lansey 2011).

Assuming the first-order approximation (Pasha & Lansey 2012), the variances of the calibrated parameters are computed based on the variances of the measured concentrations. In particular, as shown in the following relations, the variances of the parameters related to chlorine decay, P_C, and THMs formation, P_T, are estimated considering errors in chlorine and in THMs measurements, respectively:

$$\text{Var}(P_C) = \left[\left(\frac{\partial [\text{Cl}]_i}{\partial P_C} \right)_{1 \times \text{NC}} \left(\frac{\partial [\text{Cl}]_i}{\partial P_C} \right)^{\text{T}}_{\text{NC} \times 1} \right]^{-1} \sigma_C^2 \tag{7}$$

$$\text{Var}(P_T) = \left[\left(\frac{\partial [\text{THM}]_i}{\partial P_T} \right)_{1 \times \text{NT}} \left(\frac{\partial [\text{THM}]_i}{\partial P_T} \right)^{\text{T}}_{\text{NT} \times 1} \right]^{-1} \sigma_T^2 \tag{8}$$

where P_C is the considered chlorine decay parameter; P_T is the considered THMs formation parameter; $[\text{Cl}]_i$ and $[\text{THM}]_i$ are the chlorine and THMs concentrations in the measurement point i, respectively. σ_C^2 and σ_T^2 represent the variances of the chlorine and THMs measurement errors, respectively. The parameters related to chlorine decay P_C and to THMs formation P_T are reported in Table 1 for all the considered models. Different assumptions are used in the presented examples for fixing the variances of the measurement errors σ_C^2 and σ_T^2.

Applying the FOSM method, the covariance matrix of model outputs is estimated from the uncertainty of model input by approximating a function with the Taylor series expansion around the mean of the parameters and dropping the higher-order terms. Then, the covariance matrixes of the predicted THMs concentrations are estimated from the variances of the parameters as:

$$\text{Cov}([\text{THM}])_P = \left[\left(\frac{\partial [\text{THM}]_i}{\partial P} \right)_{N \times 1} \text{Var}(P) \left(\frac{\partial [\text{THM}]_i}{\partial P} \right)^{\text{T}}_{N \times 1} \right]^{-1} \tag{9}$$

where N is the number of the control points and P is the considered parameter. One covariance matrix of THMs concentrations is computed for each parameter, so they are NP. The diagonal elements of the covariance matrixes are the variances of THMs concentrations with respect to the considered parameter in the control points. The total variance of the THMs concentration prediction in each measurement point is computed as the sum of variances estimated separately with respect to each parameter. The sensitivity matrixes of chlorine and THMs concentrations with respect to the kinetic parameters are estimated analytically, considering Equations (1)–(5).

Because FOSM analysis furnishes only the variances of the THMs concentrations, assumptions on the theoretical probability distribution have to be made to interpret the output uncertainty. In the present study, FOSM outputs are assumed to follow the Gaussian distribution (Kang *et al.* 2009) and the lower and upper bounds of the prediction intervals (PIs) of the THMs concentrations are computed as the predicted value minus (plus) 1.96 times the corresponding standard deviation, which corresponds to the 2.5% (97.5%) percentile of the Gaussian distribution.

Moreover, in order to verify the applicability of the FOSM method, a preliminary analysis, described in the next section, is performed applying the MC method on a literature network with synthetic data.

EXAMPLE 1: NETWORK NET2

The Net2A network from the EPANET user's manual is adopted for the preliminary study on the FOSM applicability. The main objective of such an investigation is the comparison between the FOSM analysis and the MC method results in estimating the effect of measurement errors on THMs prediction using the first-order kinetic model. In particular, after investigating the normality of the MC results, they are compared with the ones obtained by the FOSM.

Network description and performed tests

The scheme of the Net2A network (Figure 1) consists of 35 nodes, 40 pipes, and one tank; the water comes into the
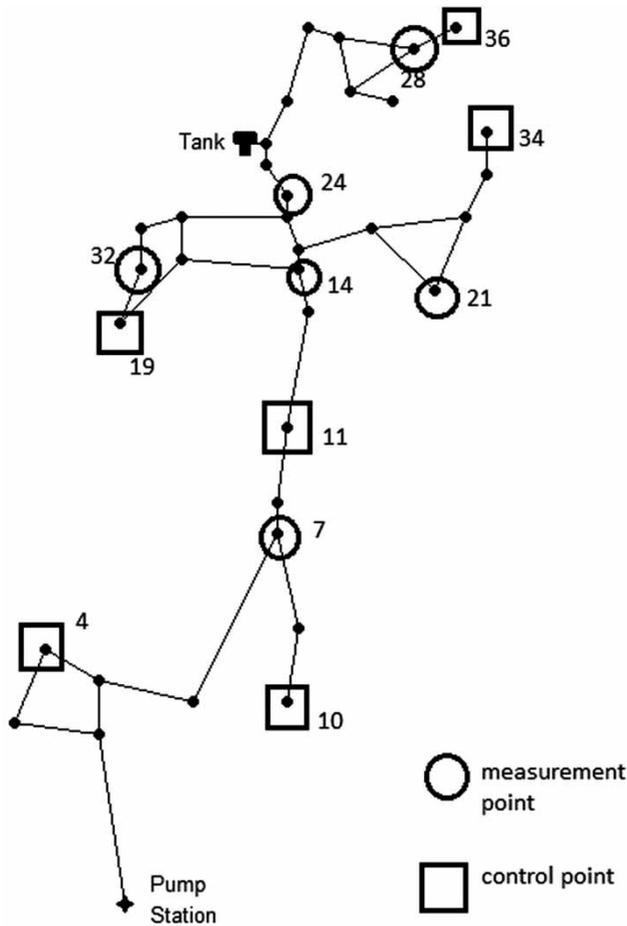
Figure 1 │ Net2A network scheme.

system directly from a pump station. Geometric data and base demands values are taken directly from the EPANET user's manual.

The disinfectant (chlorine) is assumed to be introduced at the source node (pump station) with a constant concentration of 2 mg/l. Steady-state simulation is performed with hydraulic and quality time steps equal to 1:00 and 0:05 hours, respectively. A 92 hour simulation is assumed to guarantee that steady-state conditions are reached in all locations.

For calibrating the kinetic parameters, synthetic measurements of [Cl] and [THM] are generated considering $K_1 = 0.0125$ (1/h) and $D = 35$ (μg/mg) at the following six locations: nodes 7, 14, 21, 24, 28, and 32 (Figure 1).

The uncertainty analysis is performed using both the MC and the FOSM methods with a coefficient of variation (CV) = 0.15 for generating the measurement errors. In applying the FOSM method, the standard deviations of the kinetic

parameters are computed through Equations (7) and (8), where σ_C^2 and σ_T^2 are evaluated as the mean values of the variances in all measurement points, estimated as the square of the product between CV and the measured value.

The following six control points are selected for presenting the effect of measurement errors on model predictions: nodes 4, 10, 11, 19, 34, and 36 (Figure 1).

Results

To establish the number of realizations of MC simulations, preliminary runs have been conducted, revealing that 200,000 realizations are sufficient for the convergence. Moreover, the normality of the MC outputs is evaluated through the graphical inspection and the Chi-square goodness of fit test, comparing the observed relative frequency function of the predicted THMs concentrations with the Gaussian theoretical one.

Figure 2 presents the histograms and the fitted normal distribution curve of the THMs concentrations in the six control points obtained from the MC analysis. All histograms are characterized by a moderate skewness, which may be explained by the fact that the maximum THMs concentration in a node is limited by the available chlorine (Equation (1)). Points far from the source of chlorine, such as nodes 34 and 36, characterized by higher water age, show higher values of skewness.

Applying the Chi-square test at the distribution of the THMs concentrations in the control points, the normality hypothesis is accepted for all considered nodes. Since MC outputs normality is confirmed, the normal distributions defined by mean and standard deviation values from MC and FOSM analyses represent the uncertainty in the estimate of the model parameters and predictions.

The mean and the standard deviations, along with the PIs represented by the 97.5 and the 2.5 percentile, of the kinetic parameters obtained from the MC method are listed in Table 2. The true values of the parameters, used for generating the synthetic measurements, are within the PI boundaries.

Figure 3 presents in a box diagram the PIs of the THMs concentrations obtained with both the MC and the FOSM methods in the six control nodes, reported in increasing water age order. In particular, the upper and lower bounds
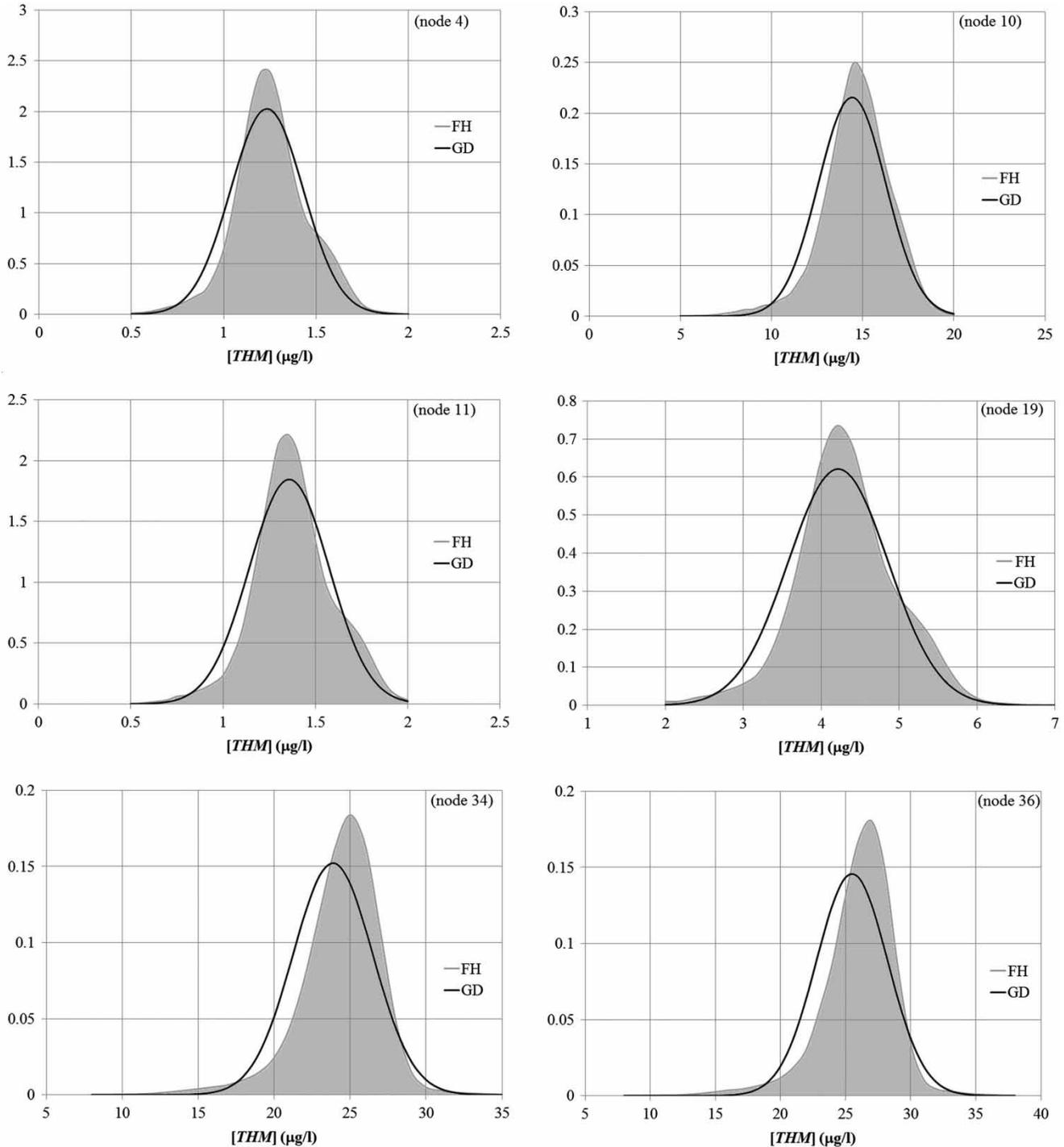
Figure 2 | MC frequency histograms (FH – gray area) and fitted Gaussian distribution curve (GD – black line) of the THMs concentrations in the control points.

of the boxes represent the 97.5 and the 2.5 percentile for the MC and the mean value plus (minus) 1.96 standard deviation for the FOSM. From Figure 3, it can be noted that uncertainty increases with the water age and that the PIs obtained using the FOSM approach are systematically wider than the ones predicted by the MC method.

Table 2 │ Model parameters uncertainty analysis results from MC

Model parameters	K_1 (1/h)	D (µg/mg)
Mean value	0.0156	30.6
Standard deviation	0.0050	6.9
PI – lower boundary	0.0058	17.2
PI – upper boundary	0.0255	44.1

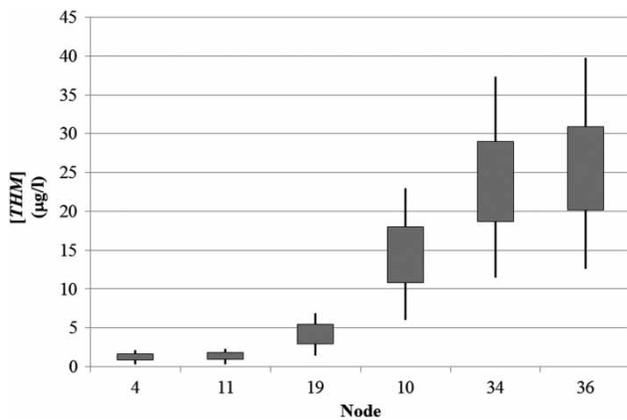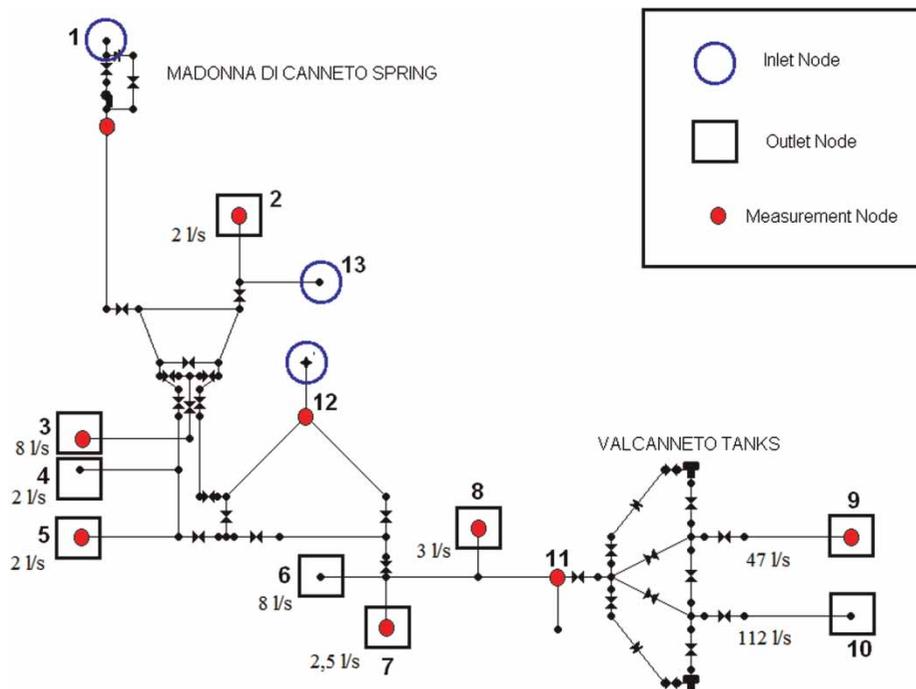**Figure 3** │ PIs of the THMs concentration in the control points (boxes, MC; lines, FOSM).

In conclusion, the normality of the MC results confirms the applicability of the first-order approximation. Moreover, in the presented example, the FOSM method, overestimating the PIs of the THMs concentration, furnishes a conservative estimation of the model predictions uncertainty.

EXAMPLE 2: THE REAL CASE STUDY OF THE AVWSS

In this example, the performances of the first-order, the second-order, and the two-phase kinetic models applied to a real case study are compared. The effect of measurement uncertainty on their predictions is also investigated.

Network description and performed tests

The considered case study is the main trunk of the AVWSS located in the Lazio region in southern Italy. It serves about 110,000 inhabitants, divided into 25 towns. The AVWSS scheme, reported in Figure 4, is composed of one reservoir (Madonna di Canneto Spring), 70 junction nodes, 51

Figure 4 │ AVWSS network scheme.

pipes, 28 regulation valves, and two tanks (ValCanneto tanks), which provide water to the internal distribution networks. The water comes into the system from the primary source of the Madonna di Canneto Spring (node 1), connected to the annex reservoir, and from two secondary inputs in the junctions Forestelle (node 13, $Q_{13} = 22$ l/s) and Cippone-Collelungo (node 12, $Q_{12} = 24$ l/s), as shown in Figure 4. The nine output junctions, along with the relative demands, are also reported in Figure 4. The hydraulic parameters were previously calibrated using tank levels and flow demands measurements, with the Darcy–Weisbach as resistance formula (Russo Spena & Vacca 1998).

Water disinfection is carried out using sodium hypochlorite (NaOCl) before the water enters into the system. A campaign of water quality measurements was realized during a period in which the hydraulic behavior of the system can be considered steady. All realized measurements are described in detail by Di Cristo *et al.* (2013), while Table 3 reports only the data used herein, represented by the residual HOCl, indicated as chlorine [Cl], and the total THMs concentrations, measured in the nine nodes indicated in Figure 4. For each measurement node, Table 3 also reports the water age, evaluated performing a 48 hour hydraulic simulation with a time step of 300 s. Because nodes 1, 2, and 12 are just downstream of the water inflow points, the measurements in them are used for assigning the initial concentrations of chlorine $[Cl]_0$ and trihalomethanes $[THM]_0$. In fact, even if in Equation (1), it is usually assumed that $[THM]_0 = 0$, this is not the case for the presented study, since no zero THMs concentrations have been measured in the inlet nodes 1 and 2 (Table 3). The other values are used for the calibration of the kinetic parameters, which is then performed with NC = 4 and NT = 6. The water quality simulations are realized with a 60 s time step.

The uncertainty analysis is performed using the FOSM method for evaluating the standard deviations of the calibrated parameters and the PIs of the THMs concentrations of the three considered models. The standard deviations of the kinetic parameters are computed, evaluating the variances of the measurement errors as:

$$\sigma_C^2 = \frac{f_C}{NC - 1} \tag{10}$$

$$\sigma_T^2 = \frac{f_T}{NT - 1} \tag{11}$$

f_C $(mg/l)^2$ and f_T $(\mu g/l)^2$ being the sums of the squared differences between the measured and simulated values after the calibration of chlorine and THMs concentrations, respectively. The coefficients of variation CV_C and CV_T are computed as the standard deviation of the corresponding measurement errors divided by the mean of the chlorine and THMs measurements, respectively.

Results

In Table 4, the calibration results of the three considered models are presented. The comparison reveals that, even if the differences among the objective function values are marginal, the two-phase model has the smallest value, which is coherent with its highest number of parameters.

Regarding the first- and second-order models, the calibration furnishes analogous D values, which are very similar to the value 41 ($\mu g/mg$) obtained by Courtis *et al.* (2009). For the two-phase model, the K_f and K_s values are within the range indicated by Sohn *et al.* (2004), with K_s smaller than K_f, indicating that the fast reaction governs within short-term ranges. The values of K_a and K_b are smaller with respect to the ones reported in Sohn *et al.* (2004), which may be explained by the lower water temperature of the considered case study.

**Table 3** | Used data for the AVWSS case study

Node	1	2	3	5	7	8	9	11	12
[Cl] (mg/l)	0.30	0.27	0.27	0.26	–	–	0.24	0.25	0.30
[THM] (µg/l)	0.64	1.97	1.49	1.32	2.00	2.45	3.02	1.77	0.00
Age (h)	0.05	1.97	0.96	6.49	5.78	8.00	21.95	7.54	0.00

Table 4 │ Calibration and uncertainty analysis results for the AVWSS case study

|	Parameters	Calibrated value	Objective function	Standard deviation
First-order	K_1 (1/h)	0.012	0.2487	0.0032
	D (μg/mg)	40		5.2
Second-order	K_C (-)	1.019	0.2263	0.0050
	u (1/h)	-0.0003		6.8×10^{-5}
	D (μg/mg)	38		4.6
Two-phase	K_f (1/h)	0.52	0.1780	0.5990
	K_s (1/h)	0.0033		0.0028
	A (-)	0.13		0.0275
	K_a (μg/(mg h))	6.47		2.4
	K_b (μg/(mg h))	0.344		0.0613

In performing the uncertainty analysis, the values of the variances of the measurement errors σ_C^2 and σ_T^2, estimated through Equations (10) and (11) are $\sigma_C^2 = 0.4$ and $\sigma_T^2 = 0.17$ for the first- and second-order models, corresponding to coefficients of variation values $CV_C = 0.07$ and $CV_T = 0.20$. The same values are adopted for the comparison with the two-phase model. The obtained standard deviations of all kinetic parameters are also reported in Table 4. The standard deviations of chlorine decay parameters K_1, K_C, K_s are of the same order of magnitude. Smaller values of the standard deviation are obtained for the u parameter of the second-order model, while K_f has a higher standard deviation. Similar values of the standard deviation are observed for the THMs formation parameter D of the first- and second-order models. Moreover, the difference between the D values obtained through the calibration for the different models is within the uncertainty range.
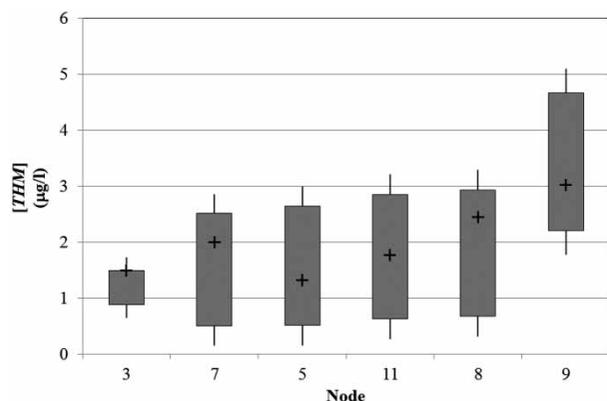
The PIs of the THMs concentrations are evaluated for the nodes in which THMs measurements are available ($N = NT = 6$). For the first-order model, Figure 5 reports the PIs of the THMs concentration considering the K_1 variance only and both the K_1 and D effects in the measurement nodes reported in increasing water age order. The PI size increases with the node water age (Table 3), with a linear law, since both the transport-decay model and the FOSM analysis are linear. The largest PI value of about 4 μg/l is reached in node 9, when both parameters are considered. The measured THMs values, also reported in Figure 5, are contained in the PIs, except for node 3.
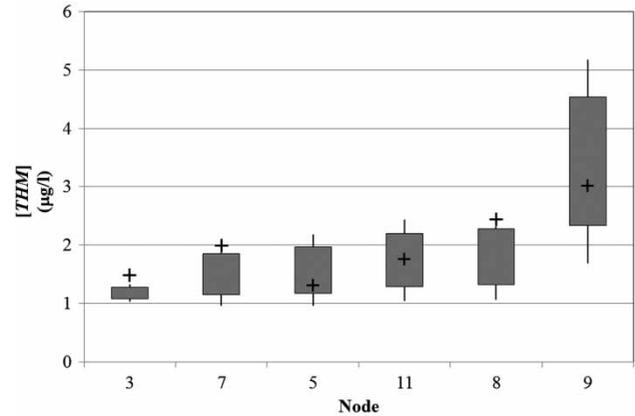
Figure 5 │ First-order model. PIs of the THMs concentration in the measurement nodes (boxes, K_1; lines, K_1 and D; crosses, measured values).

For the second-order model, in Figure 6, the PIs of the THMs concentrations are reported considering the variances of K_C and u only, along with the ones obtained taking into account the effect of all the three coefficients. In this case, the PI amplitude still increases with the node water age, but not linearly, with the widest interval of about 5 μg/l at node 9. Moreover, the higher PI values of the second-order model compared with those of the first-order indicate its minor robustness with respect to measurement uncertainty. The measured THMs values, reported in Figure 6, are in this case contained in the PIs.

For the two-phase model, in Figure 7, the PIs of the THMs concentrations are reported considering the variances of the three chlorine decay parameters K_f, K_s, A only, along with the ones obtained taking into account the
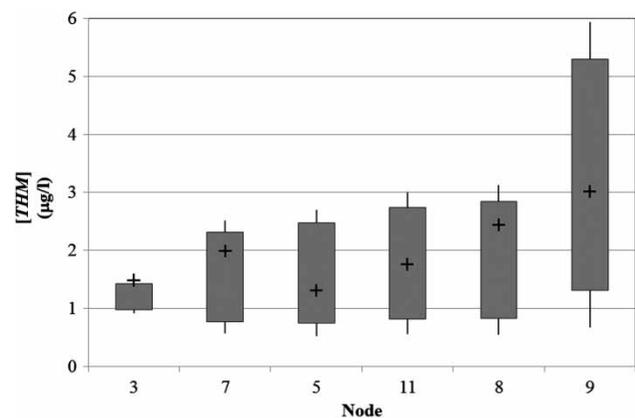
Figure 6 │ Second-order model. PIs of the THMs concentration in the measurement nodes: (boxes, K_C and u; lines, K_C, u and D; crosses, measured values).

Figure 7 | Two-phase model. PIs of the THMs concentration in the measurement nodes: (boxes, K_f, K_s and A; lines, K_f, K_s, A, K_a, and K_b; crosses, measured values).

effect of all five coefficients. The PI amplitude increases linearly with the node water age, but with two different grow rates for low and high ages, representing the different behavior of the fast and slow reactions with respect to measurement uncertainty. In particular, the growth factor decreases for age values larger than 6 hours. With respect to the first- and second-order models, the two-phase shows larger PI values in all nodes, except for node 9, characterized by a water age of about 22 h. This result suggests a minor robustness of the two-phase model with respect to the measurement uncertainty for low water ages.

CONCLUSIONS

In the present paper, the simulation of THMs formation through calibrated kinetic models is investigated, along with the assessment of the measurement uncertainty on the parameters estimate and on the model predictions. Three different kinetic models are considered and compared: a first-order model, a second-order model and a two-phase model, which considers fast and slow kinetic reactions. The effect of measurement uncertainty is mainly investigated using the FOSM method.

In order to verify the applicability of the first-order approximation, a preliminary analysis is performed using the MC method and the first-order kinetic model on a literature network with synthetic data. The normality of the MC results confirms the applicability of the FOSM method,

which in the presented application furnishes a conservative estimation of the model predictions uncertainty.

In the analysis performed on the real test case, represented by the main trunk of the AVWSS, in which the disinfection is performed using sodium hypochlorite, the kinetic parameters are calibrated through an automatic calibration procedure and the uncertainty analysis is performed with the FOSM method.

The comparison among the three considered models shows similar performances in terms of predicted concentrations, which suggests using the simplest first-order one with only two parameters. Moreover, the FOSM analysis reveals that the first-order model results in being less affected by measurement uncertainty compared with the second-order one. The behavior of the two-phase model regarding measurement uncertainty strongly depends on the water age.

Finally, the values of the THMs formation kinetic coefficient D, obtained for both the first- and second-order models are quite similar, indicating a value of about 40 ± 5 µg/mg, consistent with previous literature estimates.

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